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Development and Evaluation of an Acid Precipitation Monitor for Fractional Event Sampling with Capability for Real-Time pH and Conductivity Measurement

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16. ABSTRACT

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DEVELOPMENT AND EVALUATION OF AN ACID PRECIPITATION MONITOR FOR FRACTIONAL EVENT SAMPLING WITH CAPABILITY FOR REAL-TIME pH AND CONDUCTIVITY MEASUREMENT

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Abstract—An acid precipitation monitor has been developed that collects fractions of rain events, measures the pH and conductivity in real-time, and stores the remaining samples under refrigerated conditions. A Z-80 microprocessor controls all operations of the monitor including sample collection, sample analysis, quality control analysis, and data recording. Quality control analysis consists of analysis upon demand of a low-ionic-strength solution. The monitor was evaluated in the field and about 40 rain events were monitored. Excellent stability of the pH electrode was found under field conditions.

Key word index: Acid precipitation monitor, field pH measurements, precipitation sub-event sampling.

INTRODUCTION

Although a number of rain monitors are in operation today, the majority are designed to collect rain on either an event or a weekly basis. There have been reports of monitors that collect rain samples on a sub-event basis, with sample collection periods determined by either elapsed time or volume of rain (Gatz *et al.*, 1971; Raynor and McNeil, 1979; Asman, 1980; Coscio *et al.*, 1982; Seymour and Stout, 1983). Fewer attempts have been made, however, to design remote monitors that can collect rain events on a fractional basis, chemically analyze the samples in real-time, and also preserve the samples for later, more thorough laboratory analyses. Initially, the primary objective of this project was to use such a monitor to determine whether changes occurred in rain chemistry between collection and laboratory analysis. However, a monitor that performs the above operations also provides detailed information on temporal chemical variations in rainfall, which may be of value in the study of removal of gases and particles or the effects of rain on material damage. For example, surface reactions associated with material damage may be accelerated by the higher ionic concentrations found early in a rain event as compared with the average concentrations that would be found by analysis of samples collected from an open container.

The primary goal of this project was to design a monitor that would operate in a stand-alone configuration to collect discrete samples of rain in small increments, analyze these fractions of rain for pH and conductivity on a nearly real-time basis, and store the samples for more thorough analyses later in the laboratory. For these studies it was critical to optimize the pH electrode performance over long periods of unattended operation. Earlier experience with various prototype monitors had demonstrated difficulties with maintenance of electrode response. Because sluggish electrode performance may be encountered, even in a controlled laboratory environment, greater difficulties could reasonably be expected in the field. We particularly wanted to incorporate automatic quality control procedures to establish the validity of the pH results. During planning, it was suggested that the most effective quality control procedure would be field analyses upon demand of a solution typical of the types of samples to be measured. Because pH electrodes contaminate rain samples, it also was necessary to keep the field measurement process separate from the sample storage process.

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The most significant decision concerning the overall design was to use a microprocessor to control all activities of the monitor. Through application of microelectronics technology, a microprocessor-based system can provide intelligent control of all monitor operations and provide increased flexibility because of the ease of changing the control program. As an example, a microprocessor can play an important role in the field determination of pH by being programmed to decide when a pH measurement on a sample is complete and valid. Normally this can be a complex process because pH electrodes are known to respond at different rates depending on past sampling history and ionic strength of the solution to be analyzed. The use of a microcomputer also allows for future monitor expansions such as modern connections, whereby the instrument status or operating details can be obtained from a remote location.

SYSTEM DESCRIPTION

A brief overview of the monitor will be presented first, followed by more detailed descriptions of the various components that were selected or designed for the system. Figure 1 is a photograph of the monitor located at a field site. To help indicate the scale, the top door has been left open, and the air cylinder provides perspective. The monitor's overall dimensions are approx. $1.9 \times 0.8 \times 0.8$ m, and it weighs about 125 kg. The rain sensor and the rain cover mechanism are both mounted on top of the monitor. The main body of the monitor is divided into two major sections, the upper compartment and the lower compartment, each of which is accessible through hinged swing-open sheet-metal doors front and back. The upper compartment contains the microprocessor electronics modules and power supply, keypad and digital display, printer, pH meter, conductivity meter with two conductivity probes, two rain sample accumulation chambers, mechanical components for the rain cover, and solution containers. The lower compartment contains a modified commercial refrigerator that in turn houses the remaining components of the monitor. These include a pH measurement chamber, sample carousel with sample vials, resistance heating for temperature control, and the necessary tubing and valves for liquid flow control. Figure 2 is a diagram of the overall monitor.

In the description that follows, the microprocessor control components are presented first because they govern the operations of most of the other system components. The other components then will be discussed in the order that a rain sample encounters them when processed through the system.

An eight slot Pro-Log, Inc., Model BR 08-H card cage houses four circuit boards that make up the control unit. Power is supplied by a Pro-Log, Inc., M281-1 power supply. The processor board is a Mostek, Inc., MDX-CPU2 card that contains a Z-80 microprocessor, 6K of erasable programmable read-only memory (EPROM) for program and constant storage, 2K of random-access memory (RAM) for read/write variables, and a counter/timer circuit for generating interrupts to the microprocessor. Operation of the stored program automatically starts upon power-up.

A Pro-Log, Inc., 7504 board is employed, which uses eight 115-V a.c. opto-isolated relays for the control of a maximum of eight solenoid valves. A Pro-Log, Inc., 7303 card controls the keyboard and display functions. A 24-key keyboard with an eight-digit LED display is provided for operator control. Through software, the keys are dedicated to perform functions such as data display, data entry, and manual operation of the various parts of the monitor.

A special-purpose card was constructed with wire-wrapping techniques and is the only noncommercial card in the system. The board contains a clock chip with battery back-up that keeps track of time and date and also generates a precise 500-ms interrupt pulse that is sent to the CPU card. Part of the circuitry on this card provides the interface between the digital pH meter and the microprocessor. The interface takes a request for one of the three digits of pH data and latches the data from the meter in preparation for a read operation. Conductivity measurements also are controlled by this board. The 100-mV analog output from the conductivity meter is amplified 50 times and then read by an analog-to-digital converter.

The special-purpose card also includes three integrated circuits that sense the wet or dry state for the rain sensor and for the two level sensors that are components of the rain accumulators discussed later in this text. A relay is provided for contact closure to control a sample carousel. Finally, an interface is provided to buffer and control the output from the microprocessor to a printer.

The 6K bytes of control code are written in Z-80 assembler language. The code was developed on a Mostek FLB-80 disk-based development system. The code is designed to take advantage of the interrupt structure for the Z-80 microprocessor; the code consists of a series of interrupt service routines. The code has been block-diagrammed and is contained in the operations manual for the monitor.

A modified Aerochem Metrics sensor was chosen for this monitor because it has been used for standard week-long bulk precipitation monitors in many monitoring networks. We also chose this detector because of its reliability and our desire to make straightforward comparisons with samplers that are open only during precipitation. The raised-grid-type detector senses the presence of rain through the conductivity of the ions in the rain when a path between a charged grid and electrical ground is shorted out. After detection of rain, the grid is heated to promote evaporation to better determine the end of a rain event.

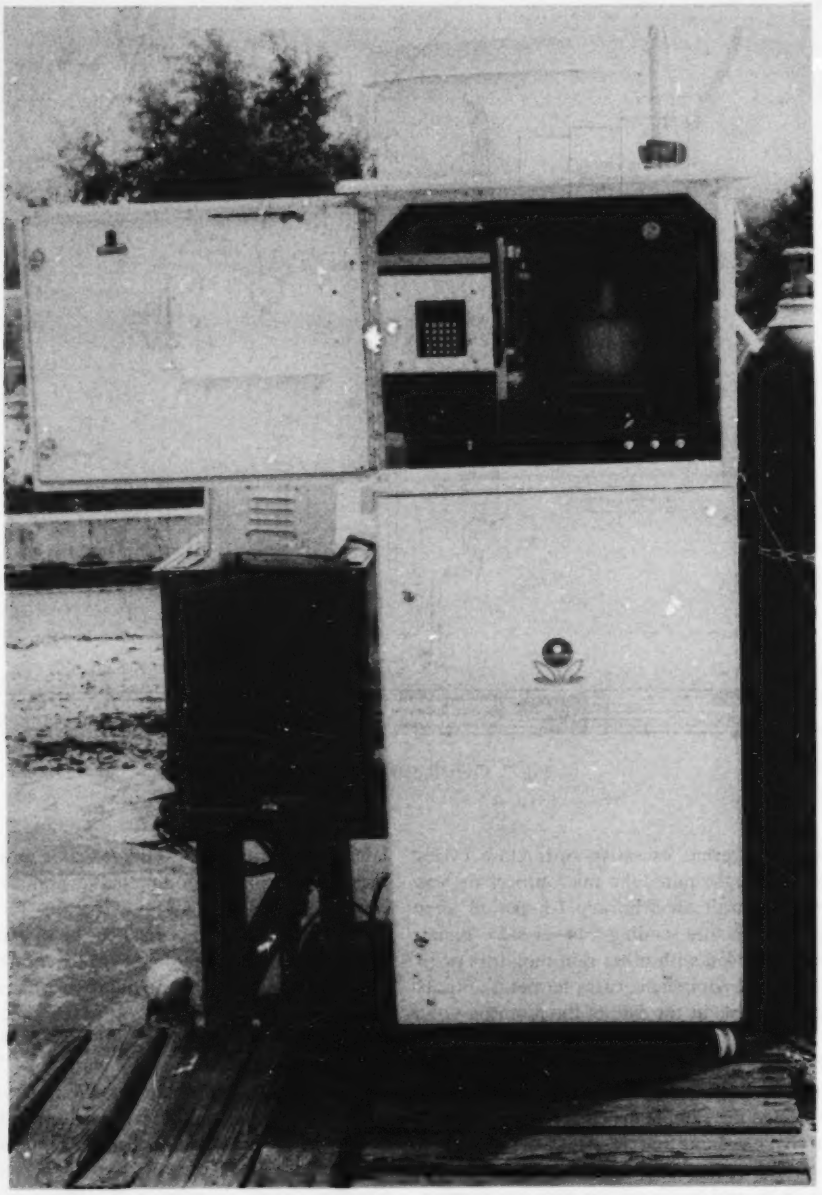

Fig. 1. View of rain monitor with upper compartment door open.

For reasons of availability and convenience at the onset of this project, a lid open/close mechanism was used that had been designed and built in the Department of Plant Pathology at the University of Minnesota (Coscio *et al.*, 1982). This cover mechanism had been used in a multi-year network study and was found to be structurally rugged and reliable. In the closed position, an 18-in. (46-cm) diameter hemispherical Teflon-coated collection funnel is covered by a tightly fitting Teflon-coated Al lid with a gasket. In response to rain detection signals from the microprocessor, a series of air-pressure-actuated pneumatic cylinders control the opening and closing of the rain cover. During opening of the rain cover, the Al lid rises, rotates away from the opening, and then drops down below the level of the opening to minimize any possible splashing. The uncovering of the opening takes several seconds and the total time for opening takes about 5 s. The high-pressure air cylinder provides the pneumatic cylinders with 45 lb of air pressure. The use of air is nominal; therefore, a single tank can be expected to last more than a year under normal

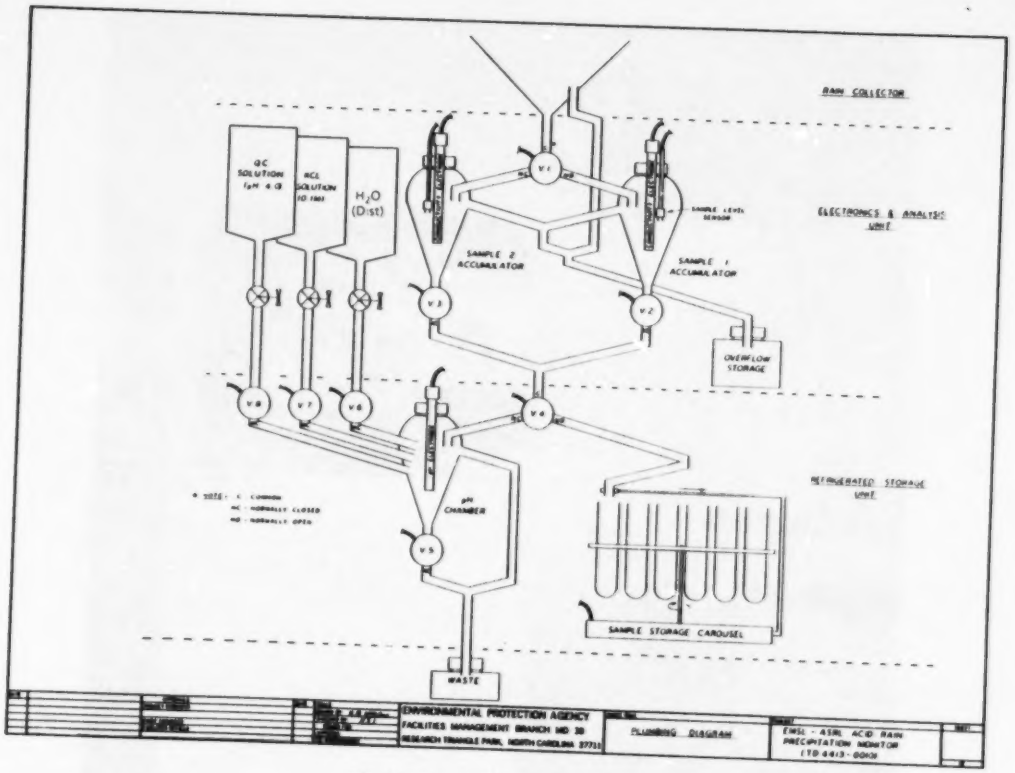

Fig. 2. Overall diagram of monitor.

conditions. To prevent excessive open/close cycles during mists or light rains, the microprocessor was programmed to wait an arbitrary 1-h period after cessation of rain before sending a cover-close signal. To allow comparison with other rain monitors or to control additional equipment, extra terminal outputs were made available at the side of the monitor.

In the design of this monitor, a compromise was reached between the degree of rain fractionation and the number of collected samples. The amount of actual rainfall collected per sample depends only on the size of the rain cover opening and the size of the individual sample containers. For this monitor, the cover diameter was 18 in. and the container capacity 50 ml. A simple calculation shows that these values correspond to one sample for each 0.01 in. of rain. Although useful for the studies that we intended, the current diameter may be too large for many applications; a smaller-diameter cover would be recommended for those cases, rather than larger containers. When all mechanical operations are taken into account, the rain sampler processes maximally about four samples per minute, which is equivalent to a rain rate of about 0.04 in. min^{-1}. For rains of greater velocity, pooling in the collector may occur. To address these rapid rains, an overflow tube was installed near the central opening in the collector so that excess rain was diverted to an overflow storage container that could be analyzed later. This addition also served as a precautionary measure to prevent flooding of the monitor in cases of power failure during a rain event.

Reliable valves are critical to the operation of the system because all liquid flows in the monitor operate by gravity action so that no pumping is required. In an earlier version of this monitor, Mace Teflon solenoid flow-through valves were used, but problems were encountered with the accumulation of particulate matter in the small passageways. During evaluation of these valves, for example, an annual spring pine pollen event led to large amounts of accumulated organic matter that clogged several valves. In addition, several problems were identified with corrosion caused by leaking tubing connections. This was particularly a problem for the valve that controlled the flow from a KCl solution storage container. To address these difficulties, we simplified the system by using Angar valves that are of a pinch-tube design. These valves are activated by 120 V a.c. and control liquid flow by compressing pliable tubing. Both two-way and three-way valves are available. A matter of some concern was the unavoidable use of non-Teflon tubing for the pliant tubing. Wherever possible, Teflon surfaces had been used elsewhere in the monitor to avoid contamination. Tests were performed on the tubing by passing deionized water through the tubing with subsequent laboratory analyses, but no contamination was ob-

served. Overall, the Angar valves performed satisfactorily. However, monthly checks of the tubing for discoloration of stiffening are recommended.

Two separate, equivalent rain accumulators are used in the monitor. Both of the accumulators and the associated tubing are mounted on an Al plate in a modular manner for ease of removal. Each accumulator vessel was constructed through modification of 125-ml Teflon separatory funnels and contains an electrical level sensor and a conductivity probe. The thin, clear walls of these vessels provide a convenient means to observe the status of the rain collection activity. The vessels were drilled near the top to accept the $\frac{1}{4}$ in. (6.35 mm) Teflon lines from valve V1. The caps were drilled to accept a feedthrough for a level sensor and a conductivity probe. The electronic level sensor consists simply of two bare wire leads separated by a small air gap that is covered when water rises in the accumulator. The electrical conductivity of the rainwater closes a circuit sensed by the integrated circuits on the special-purpose electronics board. The amount of rain collected per sample can be varied easily by altering the height of the sensor in the vessel. The sensors were adjusted to trigger after 50 ml of rain is collected. As shown in the diagram (Fig. 2), extra holes and lines were installed to catch any overflow in case of power failure.

The accumulator section operates as follows: a directional switching valve, V1, which is under microprocessor control, selects which of the two accumulators to fill. This valve initially directs all rainfall toward the first of the pair of accumulators (called Side 1) until the 50-ml level sensor is activated. The switching valve then directs subsequent rainfall toward the second accumulator (Side 2). At this time, the microprocessor directs the preparation of the pH cell (discussed below) for measurement by draining off the KCl storage solution and rinsing the electrode with deionized (DI) water. When the pH electrode is ready, the valve at the bottom of the filled accumulator (V2 or V3) is opened, and the rainwater is passed through a flow-directional valve, V4. The first 15 ml of the collected rain passes by gravity flow to the pH cell for analysis. The remaining 35 ml is directed by V4 to the storage vials for refrigeration. The relative amounts of rain passed to the pH cell and the storage vials can be controlled simply by the amount of time that the valve directs flow to the pH cell. Once the second accumulator is filled with a rain sample, either of two courses of action is available. If the pH determination of the first sample is complete, the second sample is processed in the normal fashion, as the first. However, if the pH determination of the first sample has not been completed, the entire contents of the second accumulator (50 ml) are passed through to the next storage vial. As long as the monitor is actively analyzing a sample for pH, all subsequent complete accumulator samples also are passed through to the storage vials.

Following this procedure means that some samples may not be analyzed in real-time, particularly during rapid rains. However, the collected rain sample will still be available for later laboratory analysis. The philosophy of this procedure is that an accurate and complete real-time determination of pH will be made for at least part of the samples during all events and for all of the samples during slow, steady rain events. In practice, many samples took about 1 min to reach a steady final pH value, but others took longer, particularly if the ionic content was low.

Each accumulator has its own conductivity probe, but there is a single conductivity meter. Through electronic switching, only the accumulator that is currently being filled is monitored by the meter. The microprocessor monitors and updates the output from the meter and uses the final value calculated when the level sensor is triggered. This value is reported on the printout with the other data for that given sample.

The pH cell has been shown schematically in Fig. 2. This unit and associated tubing and valves are mounted on an Al plate as a module for ease of installation and possible cleaning or repair. The main body was constructed from a modified 100-ml Teflon separatory funnel. The cap was drilled to accept an Orion 91-62-00 electrode, which is connected to an Orion Model 611 research-grade pH meter that is temperature-compensated. The bottom of the funnel was attached to an Angar pinch-valve (V5). The rain sample is delivered by $\frac{1}{4}$ in. Teflon tubing through a drilled hole on the side near the top. In addition, the body is drilled to accept three additional Teflon tubing lines. These three lines are connected to storage containers for the following three solutions: quality control solution (10^{-4} N H_2SO_4), KCl electrode storage solution, and DI water. The solution supplies are controlled by valves V6, V7 and V8, respectively.

In the standby mode, the pH cell contains a high-ionic-strength 0.1 M KCl solution. Before analyzing a rain sample, the cell is drained by valve V5, the electrode is rinsed with about 30 ml of DI water, and the sample is admitted (15 ml as stated above). The microprocessor constantly monitors and updates the value of the pH reading from the pH meter. Three successive readings at 10-s intervals must agree to within a programmed delta pH (usually 0.02 or 0.04 pH units). Once the microprocessor determines that a stable reading has been obtained, the final value is recorded, and valve V5 is opened to drain the cell to an external waste container. There is also a programmable time-out period for the pH determination. If a stable reading, as defined above, has not been reached by the end of the time-out period, the pH determination process is terminated, the final pH value is recorded, and a message stating that time-out has occurred is added to the monitor printout. At the end of sample processing for pH determination, the vessel is refilled with the KCl storage solution.

The microprocessor directs the analysis of the quality control solution at programmable intervals. It performs this analysis in exactly the same manner as it does for rainwater samples by using identical control

parameters. The output results of these determinations are sent to the printer with the appropriate information.

A commercial household refrigerator was modified to form the lower compartment. To provide protection to the microprocessor electronics, a zero-crossing circuit was constructed to switch the power on and off to the refrigerator. For storage of rain samples, an Eldex carousel was mounted in the bottom of this compartment. The carousel is under control of the microprocessor and advances after receiving each sample. Samples are kept under refrigeration until collection by the station operator. The carousel has the capacity to hold 50 sample vials of 1-in. (2.54 cm) diameter. Normally, we have used 50-ml polypropylene sample vials that can be sealed with screw caps. This carousel was chosen because of low cost but has the drawback that there is no means for the microprocessor to query the absolute vial position (i.e. there is no encoder). The lack of position encoding can be a problem in cases of power failure because the microprocessor resets the internal default vial position counter when power is restored. The rain samples continue to be delivered to the correct vials, but the printouts are incorrect.

Other components include an ASG 1100 printer from Alps, Inc. This 20-column printer was used because of its small size (2 in. × 2 in. × 8 in.) and high reliability. For conductivity, an Amber Science 1052 meter was used with paired Amber Science 1115 conductivity cells. Fans were provided in the upper compartment to protect the electronics against hot weather conditions. Light bulbs with temperature sensors and controllers were placed in both the upper and lower compartments to serve as a partial solution to low temperature environments. The practical lower temperature limit of the unit is about −3°C.

Data reports produced on the roll-paper printout include a station identification code, time of sample collection, sample vial position in the carousel, final pH and conductivity readings, and quality control solution results.

EVALUATION

Both laboratory and field testing were used to evaluate the monitor and included wet chemistry laboratory analyses of the collected solutions. The studies included Cl^-, NO_3^- and SO_4^{2-} analyses by anion ion chromatography (IC) on a Dionex Model 10 ion chromatograph; Na^+, NH_4^+ and K^+ by cation IC on a Dionex Model 14 ion chromatograph; NH_4^+ determination (alternative method) by a Technicon autoanalyzer; pH with an Orion Model 611 pH meter; and conductivity with a Cole–Parmer 1481-00 conductivity meter.

Before field deployment of the monitor, preliminary testing included the passage of various solutions through the system to ensure that their chemical content was unchanged by the monitor. First, DI water was used to show that the monitor did not contaminate samples. Second, solutions of various standards that had been obtained from a rainwater interlaboratory testing program were processed through the system. No removal of chemical species was noted.

After several iterations of minor design changes and software modifications, the monitor was deployed for field evaluation. The collection site was located on the roof of an EPA laboratory building at Research Triangle Park, NC. With the exception of several holiday periods, the monitor was operated continuously during a 9-month period from September 1985 to early July 1986. The monitor was serviced on a weekly basis, though usually it also was checked daily. In addition, it was serviced after each rain event. The routine weekly service included pH electrode calibration checks with 4.00 and 7.00 pH buffers. The pH meter span was adjusted only if necessary, but this generally was not required. The calibration of the conductivity meter was evaluated on a weekly basis with 36- and 72-μS KCl solutions. The meter required minor recalibration approximately once per month. Solution containers were checked and refilled if necessary. By operating the monitor in the manual mode, the cover opening was opened and then rinsed with DI water, which then passed through the remainder of the system. This check served to corroborate the proper mechanical functioning of the entire monitor.

In the case of rain events, the printer outputs were checked carefully against the carousel contents for volume and filling. The tape was examined for vial position agreement. The rain sample vials were capped and transported to refrigerated storage in the wet chemical analysis laboratory for same-day or next-day analysis. The carousel was reloaded with sample vials, and the carousel was repositioned to the first position.

Over part of the test period, an AeroChemetrics rain sampler was connected in parallel to the rain sensor of the real-time monitor. Plastic bag liners were used in the buckets as suggested in the literature (Eaton and Estes, 1984; Topol and Ozdemir, 1986). On a weekly basis, the AeroChemetrics samples were collected and delivered to the wet chemistry laboratory for mass determination and for aliquots for later chemical analysis. Because of the widely varying patterns and quantities of rainfall and because of the short period of time that the AeroChemetrics sampler was in use, a reliable comparison of rain volume was made for only three 1-week periods. Systematic differences were not found. A thorough investigation of the relative collection efficiencies of the open container type of collector and real-time monitors under varying wind conditions was beyond the scope of this program.

During the evaluation period, approx. 40 rain events occurred, and more than 900 vials of rain were collected (note that only the first 0.5 in. of any given rain event could be collected because of the large rain opening and the limitation of 50 vials). On numerous

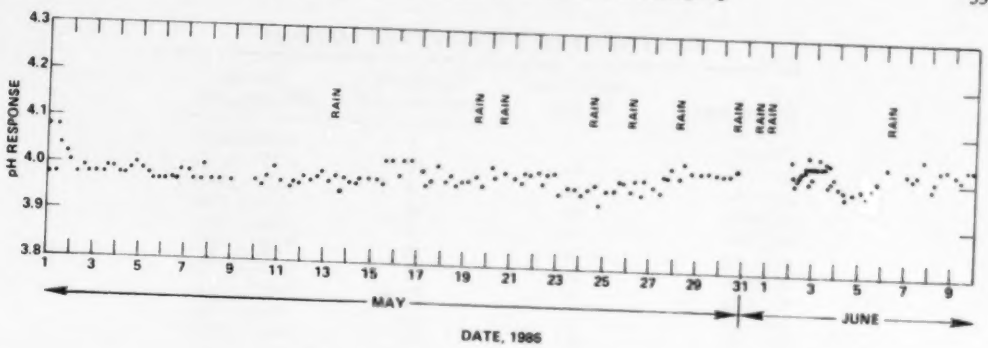

Fig. 3. Plot of quality control results vs date.

occasions, the cover opened in response to a few drops of rainfall, but there was an insufficient amount of precipitation to perform a pH measurement.

One of the primary goals of this project was to obtain and demonstrate electrode stability over long periods in a field environment. During most of the 9-month evaluation period, the monitor was programmed to analyze the H_2SO_4 quality control (QC) sample (pH 4.00) every 6 h. Occasionally, this frequency was reduced to 12 h to help minimize solution use. In addition, hourly checks were sometimes made after major instrumental changes, such as electrode replacement, or when a possible problem was suspected. Figure 3 shows a plot of the pH electrode response to the QC solution over a typical 6-week period. Periods of rain are indicated in the figure. As can be seen, this period was punctuated by a large number of rain events, although many were in fact quite small events with little measurable precipitation. The microprocessor software was set up so that the QC determination was bypassed if a rain event was in progress. Over this particular 6-week period, the QC response averaged 4.01 ± 0.05 pH units compared to the expected 4.00. A break in the values on about 31 May resulted from an electrical power failure that caused an unexpected problem that shut down the monitor. Although no electrode problems were found during the particular time period plotted in Fig. 3, on other occasions, the QC response provided an excellent indicator of actual or potential problems. In several cases, erratic readings (QC responses of 3.80–3.90 pH units) resulted from an electrode that demonstrated a sluggish response. Normal operation was resumed by cleaning the electrode frit and heating in KCl. In several other cases, abnormal readings were found to have resulted from depletion of one of the solutions. To summarize, the electrode response to the QC solution was a good indicator of the condition of the electrode for subsequent field response.

Table 1 compares the results for pH measured automatically in real-time by the rain monitor and the results for sample vials of the same rains measured later in the laboratory. This comparison covers all of the rain events for which there were at least two vials of rain collected during the period December 1985–July 1986. During normal operation, the condition parameters for the automatic field pH determination were set so that three successive measurements at 10-s intervals should agree to within 0.02 pH units. The maximum analysis time allowed before time-out was usually set for 5 min. Field pH measurements were simply read off the printed paper output. Laboratory analyses were performed as soon as possible after the samples were collected from the precipitation monitor, usually within 24 h. To construct Table 1, a value was calculated for each vial by subtracting the pH value found in the laboratory from the pH value found in the field. These difference values were then arithmetically averaged for all the samples of each rain event, and a standard deviation was calculated. Although averages of pH values do not have any particular chemical significance, they provide a convenient qualitative indicator of electrode performance. With the exception of two rain events, the agreement was considered satisfactory: agreement was within about 0.05 pH units. Larger deviations (0.2–0.3 pH units) were found for two events with rather low acidity, $pH > 4.5$ for all samples. As also indicated by the conductivity response, these samples possessed low ionic strength, which is known to lead to a sluggish response.

Figure 4 allows an evaluation of the monitor's performance in the measurement of conductivity. More than 400 rain sample vials that had been recorded and analyzed in the field were analyzed later in the laboratory. Because of the particular conductivity meter used in this model of the precipitation monitor, the highest value that could be reported in the field was 100.0 μS; consequently, any data with exactly this reported value were not plotted because the actual conductivity may have been substantially higher. Overall, the agreement shown in Fig. 4 is good, to within 15% in the middle of the scale and above. It should be noted that the scatter in the data arises from the combined errors of the field and laboratory measurements. In about 2% of the cases, unusual differences were found. In some of the cases in which the laboratory found values significantly > 100 μS (as high

Table 1. Field monitor vs laboratory pH comparison

Date of event	No. of vials for event	No. of vials analyzed in lab	Average difference ± SD
12/12/85	7	5	0.052 ± 0.031
12/13/85	49	19	0.257 ± 0.122
01/03/86	10	4	0.035 ± 0.072
01/19/86	36	15	0.265 ± 0.597
01/25/86	12	9	0.086 ± 0.051
02/10/86	28	20	0.064 ± 0.059
03/13/86	49	17	0.010 ± 0.120
03/14/86	43	22	0.067 ± 0.114
03/19/86	50	5	0.002 ± 0.064
03/27/86	27	27	0.047 ± 0.038
04/07/86	10	8	−0.010 ± 0.043
04/21/86	30	20	−0.014 ± 0.034
04/26/86	50	18	−0.034 ± 0.050
05/13/86	7	4	−0.003 ± 0.043
05/20/86	50	20	−0.042 ± 0.129
05/20/86	13	5	0.046 ± 0.019
06/07/86	50	11	0.011 ± 0.043
06/28/86	43	17	0.055 ± 0.033
07/02/86	11	3	−0.013 ± 0.116
07/10/86	37	10	−0.006 ± 0.053

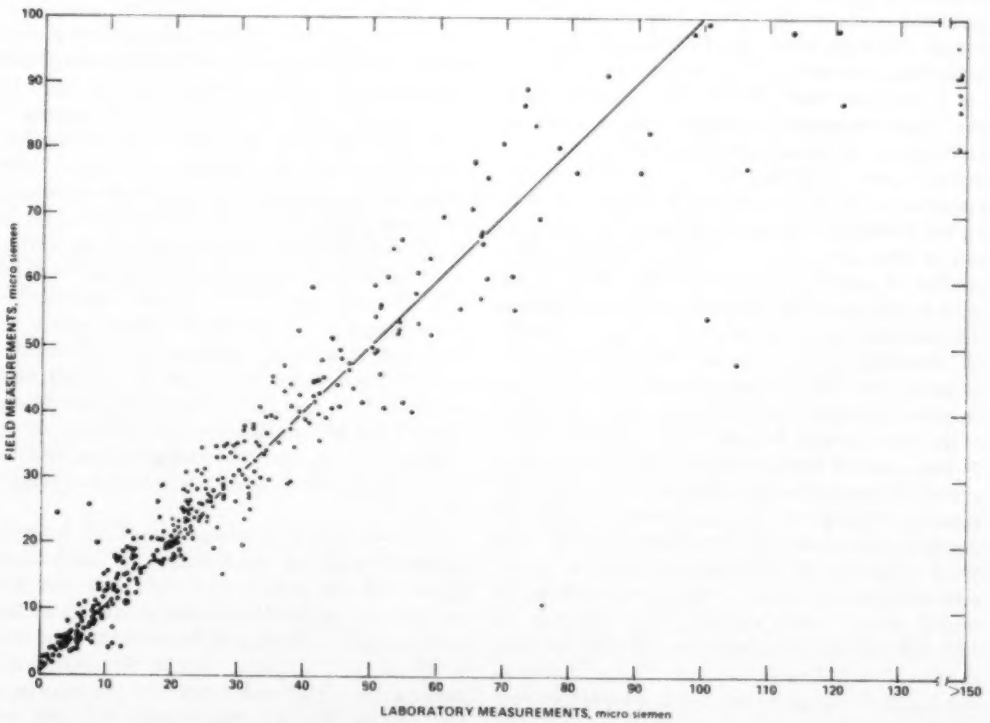

Fig. 4. Comparison of field and laboratory conductivities for collected rain samples.

as 300 μS in a single case), a value < 100 μS was reported by the field monitor. Two explanations appear plausible: (1) coarse particles or organic aerosols could have been washed out by the rain, but took a significant time to dissolve and release their ionic content to the collected rain water, or (2) there was inefficient mixing in the accumulator during the rain and that the very acidic first droplets did not become mixed well. Because of the geometry of the accumulator and the position of the probe near the top of the

accumulator, it is possible that the probe was recording the rain sample as more clean than the average value for the sample.

For general observations during the evaluation, the results from the automatic quality control solution analysis and the results from the laboratory-to-field comparison demonstrate that the pH electrode showed excellent response. By comparing these results with those from earlier monitors designed and tested in these laboratories, the KCl storage solution seems to make the difference. There were a number of power interruptions during the evaluation phase; however, the non-interruptable power and memory features worked well as demonstrated by successful recovery and continued operation. One deficiency of the current monitor is the lack of cold weather capability. There are temperature-controlled heaters for both the electronics compartment and the refrigerator compartment, but they are inadequate below approx. −5°C. At this temperature, solutions may freeze. Finally, there are concerns about the method for handling overflows during very heavy rain events. The excess water in the cover is diverted to an overflow, but there is no monitoring of this activity.

OBSERVATIONS

The time fractionation capabilities of the monitor allow examination of rain events in a detailed manner. We present here several observations of rain events that occurred during the monitor evaluation period from October 1985 to July 1986. We must emphasize that the observations that we present are mostly qualitative because a comprehensive study of rainfall was not part of the mission of this project. To interpret the results in detail, it would have been necessary to obtain meteorological data covering the time period of interest, and it would have been helpful to have obtained data on the aerosol and gas species present in the air before and during the rain events.

Figure 5 shows the pH and conductivity results vs vial number for the rain event of 22 October 1985. The vial number position corresponds directly with the total rainfall, with each vial representing about 0.01 in. of rainfall. The laboratory and field results for conductivity and H^+ concentration are compared for these two parameters. Figure 6 shows concentrations of some of the other important ions as a function of rainfall for that event. Quite often, initial samples showed high ion levels and succeeding samples showed lower levels. This may demonstrate a washout phenomenon, which could be expected if the falling rain scavenges aerosol particulate matter and gases.

Figure 7 shows a rain pattern for 10 February 1986. This was a rather light rain in which two samples were initially collected at 3:00 p.m., followed by very light intermittent rain over the next 8 h. The monitor was programmed for a 1-h wait period after the cover closed to ensure that the rain was actually over. Vials

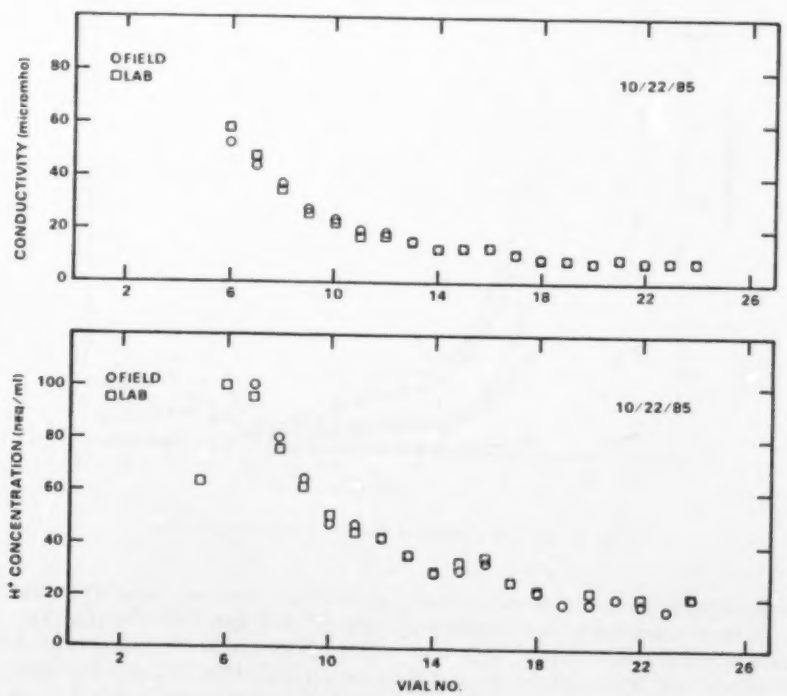

Fig. 5. H^+ Concentration and conductivity during typical rain event.

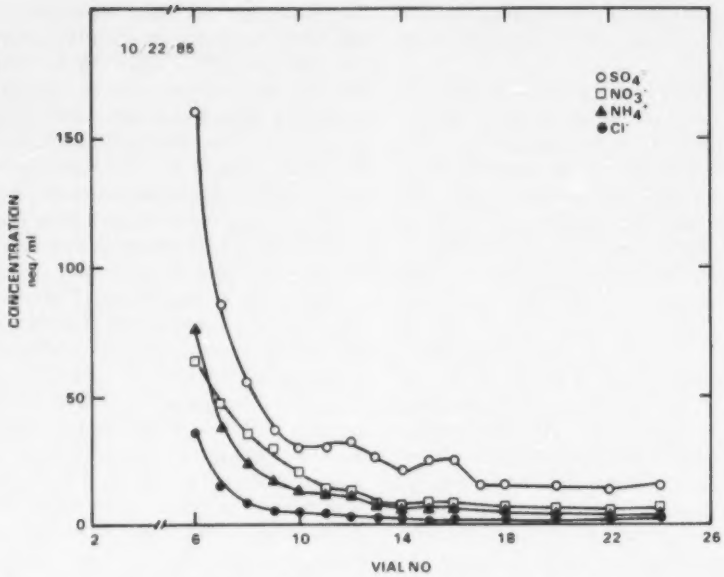

Fig. 6. Chemical analysis of typical rain event.

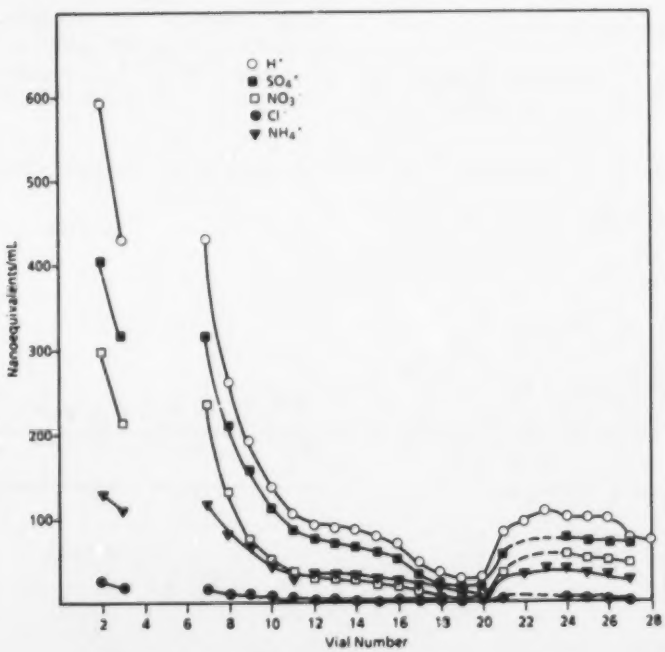

Fig. 7. Chemical analysis of event of 10 February 1986.

4–6 represent incomplete vials during the intermittent rain period. In these cases, there was insufficient sample to make chemical measurements. Light rain started at 11:00 p.m. and continued for about 1 h (vials 7–20). During this 1-h time period, the frequently found decrease of ionic concentrations with sample number was observed. Another break in the rain occurred, and then several samples were taken from 3:00 to 5:00 a.m. At this time, the plot shows that the ionic content of the rain increased again. A slightly more complex behavior is shown in Fig. 8. Overall, there is the same decrease in concentration with time,

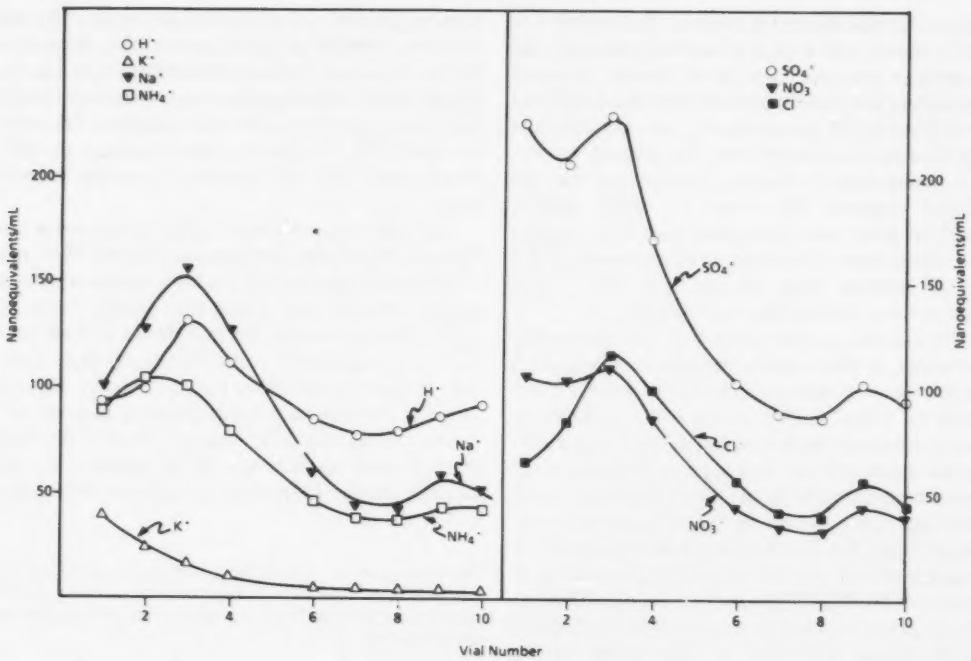

Fig. 8. Chemical analysis of event 21 April 1986.

but it is not as dramatic as that exhibited by the earlier examples. Some sample ion species increased in concentration with time.

During the deployment period, the most acidic individual vial field reading had a pH value of 3.21, and the least acidic sample had a pH of 6.14. The highest laboratory conductivity value recorded over this time was 317 μS.

As indicated earlier in the evaluation section, we also measured acidity and conductivity in the laboratory for the majority of the field samples. In a number of cases, we measured Cl^-, NO_3^- and SO_4^{2-} by IC; NH_4^+ by autoanalysis; and, in some cases, Na^+, K^+ and NH_4^+ by cation IC. Rudimentary conductivity calculations were performed with the measured ion concentrations to compare with the laboratory and field conductivity measurements. However, these calculations did not provide much additional information because most samples were rather acidic. For acidic rainwater samples, H^+ provides the predominant contribution to the conductivity. Consequently, reasonable agreement was found even when all ions were not analyzed.

As a final generalization, no systematic differences in pH or conductivity were found between laboratory and field measurements. This observation addresses one of the primary goals of the project: the assessment of possible chemical changes of rain samples between time of collection and laboratory analysis. However, it is certainly possible that some species such as organic acids may undergo changes. In view of the above observation, there does not appear to be a pressing requirement that pH and conductivity be measured in real-time in the field, and these measurements can await laboratory analysis. On the other hand, removal of the requirement for storage of each rain fraction would allow the analysis capabilities of the monitor to be exploited further. Conductivity and pH of rain could be analyzed automatically in increments as small as desired. With the present monitor design, conductivity would be measured on each small fraction, and pH would be measured on as many of the samples as the pH measurement cycle time allowed. These data would provide detailed information on the time progression of rain events and could be related to meteorological observations.

SUMMARY

Overall, the precipitation monitor worked well during the evaluation period for the collection of fractions of rain events and for the analysis of the samples for pH and conductivity. The difference between field and laboratory pH measurements was approx. ± 0.05 pH units for samples in the pH range of 3.5–4.5 pH units. The difference between field and laboratory conductivity measurements was about $\pm 15\%$ for samples in the 20–100-$\mu\Omega$ range.

The primary accomplishment of the project was the successful utilization of microprocessor technology to control all operations of a sophisticated monitor in a

stand-alone environment in the field. The monitor was able to operate over a range of weather conditions and to continue operation after power failures. A second accomplishment was the development of a design that ensured successful operation of a pH electrode over long periods of time in the field. The frequent analysis of a quality control solution demonstrated that the monitor response was stable to within approx. ± 0.05 pH units over month-long periods. Compared with results from earlier monitor designs, most of this success stemmed from the use of a KCl storage solution when the monitor was inactive.

Although the monitor works well as a stand-alone instrument, it does require periodic servicing. As a matter of good quality control, we recommend that it should be visited weekly to check the levels of the various solutions, retrieve samples, check the quality control results on the data tape, and calibrate the meters, if necessary. If the monitor is to be used on an event basis, these actions can be conducted on a more frequent basis. The use of the solutions depends on the frequency of both rain events and programmed quality control analysis. During our evaluation with twice-daily QC analyses, the solutions lasted for more than a month. As suggested earlier, the rainwater flow tubing should be checked monthly for discoloration or stiffening. Replacing the tubing is a simple matter that was done twice during our 9-month evaluation.

Adaptations of these monitors are now in use in two different studies. Our monitor has been modified for use in the Mountain Cloud Chemistry Program co-sponsored by the U.S. Forest Service and EPA. For this adaptation, the cover mechanism has been disabled, and samples are instead provided by the output from cloud water string collectors. This monitor has gathered data at a field site on Mount Mitchell, NC. As a part of a study by the Illinois State Water Survey, a second monitor has been largely simplified so that it only fractionates rain events, measures conductivity, and stores the samples for later laboratory analysis.

RECENT IMPROVEMENTS

After the original evaluation period ended in July 1986, several significant modifications and improvements were incorporated. The earlier air-actuated rain cover mechanism was eliminated and replaced by one that is powered by an electric motor. Also, the area of the new rain cover has been reduced by about a factor of three to accommodate rain events with large rainfall rates. A conductivity meter with a range of 200 μmho was used. This conductivity meter provides an additional output; the measurement of sample temperature.

One improvement that is being considered is the addition of auto-answer modern capability. With this addition, the status of the monitor, results of quality control analysis, and recent rain history could be queried from a remote location. More sophisticated carousel mechanisms are becoming increasingly available. The use of a sample carousel that allows collected samples to be revisited would permit a different and more complete sampling strategy. Further development possibilities that are being explored for the monitor include adaptations to sample snow events and dew events.

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